

UNCLASSIFIED

AD NUMBER
AD814722
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to DoD only; Administrative/Operational Use; APR 1967. Other requests shall be referred to US Army Electronics Command, Attn: AMSEL-KL-FE, Fort Monmouth, NJ 07703-5601.
AUTHORITY
US Army Electronics Command ltr dtd 1 Aug 1967

THIS PAGE IS UNCLASSIFIED

AD

TECHNICAL REPORT ECOM-01291-7



REVERSIBLE OXYGEN ELECTRODES

7TH QUARTERLY REPORT

By

J. O'M. Bockris

M. Genshaw

E. A. Beer

D. Sepa

Y. C. Chiu

April, 1967

ECOM

UNITED STATES ARMY ELECTRONICS COMMAND • FORT MONMOUTH, N.J.

CONTRACT DA28-0-3-AMC-01291(E)

UNIVERSITY OF PENNSYLVANIA

The Electrochemistry Laboratory, Philadelphia, Pa. 19104

Distribution Statement

Each transmittal of this document outside the Department of Defense must have prior approval of CG, U. S. Army Electronics Command, Fort Monmouth, N. J.
ATTN: AMSEL-KL-PE

AD814722

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official Government indorsement or approval of commercial products or services referenced herein.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

REVERSIBLE OXYGEN ELECTRODES

Report No. 7

Contract No. DA 28-043-AMC 01291 (E)

Task No. 1 CO 14501 A34A-00

SEVENTH QUARTERLY REPORT

For the Period

15 October 1966 - 14 January 1967

U. S. ARMY ELECTRONICS COMMAND

Fort Monmouth, New Jersey

Object: To conduct research on electrocatalysis, to determine the mechanisms of oxygen reduction and to find the major factors affecting the catalytic activity of the reaction so that a reversible oxygen electrode may be developed.

Prepared by D. Sepa, Y. C. Chiu, E. A. Beer and M. Genshaw

Under the Direction of Professor J. O'M. Bockris, Principal Investigator

The Electrochemistry Laboratory
The University of Pennsylvania
Philadelphia, Pa. 19104

DISTRIBUTION STATEMENT

Each transmittal of this document outside the Department of Defense must have prior approval of CG, U.S. Army Electronics Command, Fort Monmouth, New Jersey. ATTN: AMSEL-KL-FE

TABLE OF CONTENTS

TITLE PAGE	1
TABLE OF CONTENTS	11
PURPOSE	111
ABSTRACT	1v
PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES	v
I. CATALYSTS FOR OXYGEN ELECTRODE REACTION	1
1. Introduction	1
1.1 Preparation of substances	1
1.2 Electrode for powder-like electrocatalysts	2
2. Experimental	3
3. Results	3
4. Proposal for future work	4
II. REDOX CATALYSIS	4
1. Introduction	4
2. Experimental	5
3. Results	6
4. Discussion	7
III. THE DETERMINATION OF CATION ADSORPTION IN THE OXYGEN REDUCTION IN ALKALINE SOLUTION	8
1. Introduction	8
2. Experimental	9
3. Results	10
4. Plan for the Future	11
IV. REFERENCES	13
V. PROJECT PERSONNEL	14
VI. FIGURES	16
VII. DISTRIBUTION LIST	

PURPOSE

One of the pressing aims at present in the development of technologically successful energy conversion in electrochemical fuel cell systems is the finding of electrode materials on which, under given experimental conditions, the process of cathodic dissolution of oxygen can function sufficiently rapidly. The eventual objective of the study on oxygen electrodes is a "reversible oxygen electrode," i.e. one which works at a sufficient rate and a negligible overpotential.

The experimental program has been designed to determine the mechanism of oxygen reduction at various experimental conditions, and to find the major factors affecting the catalytic activity of the reaction. For this purpose, the O_2 reaction is studied on a number of metal electrodes and on various compounds stable in acid solutions and at high electrode potentials.

ABSTRACT

Small crystals of lithium, potassium and cesium tungsten bronzes were prepared. Also nonstoichiometric γ -tungsten trioxide was prepared. To study the catalytic activity of these bronzes a method of sintering them into gold was devised.

The homogeneous oxidation of iodide by oxygen was studied. The rate constant at 25° is $4 \times 10^{-5} \text{ sec}^{-1}$. The reaction is first order in oxygen and zero order in iodide and hydrogen ions. The activation energy is 16.9 kcal/mole.

A very sensitive method of determining ion adsorption utilizing multiple reflection ellipsometry is suggested.

PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES

A. Publications

A. Damjanovic, M. A. Genshaw and J. O'M. Bockris, "Distinction Between Intermediates Produced in Main and Side Electrode Reactions", J. Chem. Phys., 45, 4057 (1966).

B. Reports

Quarterly Reports Nos. 1 through 6 on "Reversible Oxygen Electrodes," Contract No. DA 28-043 AMC-01291(E).

C. Conferences

5 January 1967
The Electrochemistry Laboratory
University of Pennsylvania
Philadelphia, Pa. 19104

Present at the conference were Mr. J. A. Christopoulos of the U.S. Army Electronics Command and Dr. A. Damjanovic, Dr. M. Genshaw, Dr. E. Beer, Mr. D. Sepa, Dr. Y. C. Chiu of the Electrochemistry Laboratory.

The experimental results of the last quarter and present plans of the project were discussed.

I. CATALYSTS FOR OXYGEN ELECTRODE REACTION

1. Introduction

In attempts to solve why tungsten bronzes are catalysts for the oxygen reduction reaction, tungsten bronzes with other alkali metals, besides sodium, as well as bronzes of some other transition metals have to be investigated. However, all of these substances are available in the form of small crystals or powders, so a new type of electrode should be designed, which would enable examination of these materials as electro-catalysts for the oxygen reduction reaction.

1.1 Preparation of substances

Crystals of lithium, potassium and cesium tungsten bronzes were prepared by electrolysis of molten mixture of WO_3 and respective alkali tungstate, in a platinum crucible, at temperatures between 700 - 800°C, using a gold wire as cathode, on which these compounds were grown, at estimated current density of about $10^{-2} \text{ A cm}^{-2}$. The anode was a cylinder of gold sheet. Bronzes which resulted from these syntheses were in the form of very loose aggregates of small crystals, which separated completely through successive washing in hot solutions of 1 M NaOH and 1 M $HClO_4$.

Nonstoichiometric γ -tungsten trioxide was prepared also, using the thermal method of synthesis and solid state reaction between tungsten and tungsten trioxide. γ - WO_3 with a range of composition $WO_{2.65} - WO_{2.76}$ has low resistivity (0.336 - 0.114 ohm cm., respectively) and is insoluble in acids, as is WO_3 . Powders of WO_3 and tungsten were mixed in a ratio that corresponded to composition $WO_{2.7}$. The homogenized mixture of powders was pressed into a pill and put in a nickel boat in the furnace. Purified

argon atmosphere was held in the furnace, heated at 800°C, during 24 hours. After cooling in the stream of argon, violet $WO_{2.7}$ was the result of synthesis.

Strontium niobium bronze and barium tantalum bronze were synthesized and kindly sent us from the Coal Research Center, Pittsburgh, United States Department of Mines. Sodium molybdenum bronze and sodium vanadium bronze were prepared in the Institute for Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia.

1.2 Electrode for powder-like electrocatalysts

Since all materials available were either powders or in the form of small crystals, they could not be examined in the same way as sodium tungsten bronzes were.¹ Therefore, an electrode had to be designed which would enable investigation of electrochemical properties of such powder catalysts.

It is known that gold is a very poor catalyst for the oxygen reduction reaction, but is very stable in acid media, especially if not oxidized. Using these properties of gold it was decided to press or sinter homogenized mixture of gold powder and the catalyst which is available in powder form. Gold powder, taken in excess, would surround very intimately grains of the substance investigated, and made excellent contact with them. By subsequent polishing or controlled dissolution of gold on the surface of such an electrode, a definite area occupied by the powdery substance would be opened, and catalyst could come in contact with electrolyte. Ratio of areas substance-gold on the surface of such an electrode could be easily determined under microscope on a representative

piece of surface, and the total area of substance calculated.

Using very wide possibilities of sintering technique, a porous electrode can also be prepared in a similar manner.

2. Experimental

A mixture of gold and sodium bronze powder, in volume ratio 2:1 was pressed in a mold of specially hard steel (Fig. 1). Pressing was performed without heating, at room temperature, due to softness of gold and non-oxidized surface of gold. Using pressures from 4.5 - 9.3 t cm⁻², excellent samples, concerning mechanical properties, were obtained.

3. Results

Higher pressure of pressing gives a sample with lower porosity. Less porous electrodes are more favorable because active area of surface could be equated to the calculated ratio of active substance in geometric area of electrode. For example, sample which was pressed with 9.3 t cm⁻², after one hour immersion in water, gained 0.75% of its weight, which, calculated to empty volume due to open pores, makes 5% of total volume. Experiment with pure gold powder, which was pressed with 7.0 t cm⁻², gave only 3% of volume filled with water (better packing of gold grains), but comparing densities of pressed sample and pure gold discrepancy was about 25%, which proves existence of closed pores inaccessible to the solution. The observed porosity of samples would not affect real working area of the electrode, because rate of reaction in pores would be strongly diffusion limited and cannot affect observed rate of reaction.

4. Proposal for future work

First sample electrode with sodium tungsten bronze of known activity is just under investigation of electrochemical behavior.

Using the same type of electrode powders of Li_xWO_3 , K_xWO_3 , Cs_xWO_3 , $\text{WO}_{2.7}$, Na_xMoO_3 , $\text{Na}_x\text{V}_2\text{O}_5$, Sr_xNbO_3 and Ba_xTaO_3 will be examined.

II. REDOX CATALYSIS

1. Introduction

The aim of this project is to improve the activity of the oxygen cathode by adding an intermediate to the electrolyte and thus changing the mechanism of oxygen reduction. The intermediate must be a redox system.

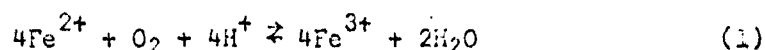
As discussed in a previous report² there are three basic requirements for this action. The chosen redox couple must

- a. have a high redox potential
- b. undergo reduction at the electrode at a high rate
- c. react with oxygen readily.

Early experiments and literature data show that it is possible to find redox systems that satisfy the first and second requirements. But all of these systems react with oxygen too slowly. Therefore the third point is the most crucial one of all three and research work should be concentrated on it.

For this reason in the previous quarter the homogeneous oxidation of several redox couples was investigated. In particular, results

concerning the kinetics of the reaction



was presented.

Keeping the emphasis on the homogeneous oxidation, during this present reporting period an attempt was made to elucidate the kinetics and mechanism of the oxidation of the redox system I^-/I_2

2. Experimental

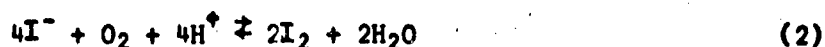
For the measurement of oxidation rates the gas-volumetric apparatus introduced earlier³ was used. It was designed to make possible the observation of all reactions involving the consumption or evolution of oxygen (or another gas). Its limitations include the inability to measure reactions with two gaseous species; but these process are a priori of no interest to the project.

Also the rate of reaction must be within certain limits if the mentioned apparatus is to be applied successfully. Processes consuming or producing less than about $3 \cdot 10^{-9} \text{ mol l}^{-1} \text{ sec}^{-1}$ oxygen do not yield sufficiently precise results; but these are too slow for catalytic purposes in any case. Reactions faster than about $10^{-6} \text{ mol l}^{-1} \text{ sec}^{-1}$ (in terms of O_2 consumption) are also hard to follow, but by adjusting the experimental conditions (mainly concentration and temperature) even these can be measured.

The oxidation of KI does not approach any of the limitations mentioned above, therefore no difficulties were encountered.

3. Results

The equation for the oxidation of KI is



The rate constant of the reaction at 40°C is $k_2 = 4 \cdot 10^{-5} \text{ sec}^{-1}$, as calculated for a first order reaction.

The reaction is first order in respect to the partial pressure of oxygen, as Fig. (2) shows. The order of reaction in respect to the hydrogen ion concentration is close to zero for pH 0.2 to 2.3 and first order for pH > 2.3 (Fig. 3).

In respect to iodide ions, the reaction is also near zero order.

Thus the overall order of the reaction appears to be 1 at hydrogen ion concentrations above 0.01.

From measurements of the rate constant at different temperatures (Fig. 4), we can calculate the activation energy of the reaction using Arrhenius' equation. For the homogeneous oxidation of potassium iodide it is $E_A = 16.9 \text{ kcal/mole}$.

A set of experiments was made to determine possible catalytic activity of activated charcoal on this oxidation process. At 40°C in a 6 M KI solution (pH=0.3) the rate constant increased four times upon addition of 1 g/l activated charcoal.

The investigation of the system is not yet finished, more points are needed to ascertain the correctness of the above data. Particularly important are further measurements with possible catalysts.

4. Discussion

The basic problem presented by the highly irreversible oxygen electrode is a kinetic one. In the oxidation process of several redox couples there is a very slow rate-determining step. As a result, oxygen practically does not oxidize its more negative neighbors in the table of standard oxidation potentials, although thermodynamic considerations lead us to expect this.

The mechanisms of these reactions do not necessarily consist of the same steps, but the fact that no oxidation could be observed with systems having a redox potential higher than about 0.8 V ($E_0 = 1.23$ V for OH^-/O_2) confirms the speculation that the same high-energy step is involved in all of these cases.

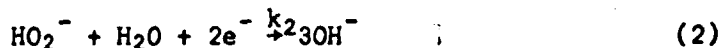
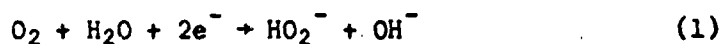
A very plausible suggestion concerning the rate-determining step is that of Latimer.⁴ He points to a possible explanation by assuming that the first step of some oxidation reactions is the reduction of O_2 to H_2O_2 , for which the standard redox potential is 0.68 V. This would make impossible any oxidation by oxygen beyond about 0.7 Volt and would explain the relative slowness of the ferrous-ferric reaction reported earlier.³ It also agrees with the present data on the oxidation of KI. The I^-/I_2 system has a standard redox potential of 0.53 V. The difference between this and 0.68 V is greater than in the case of $\text{Fe}^{2+}/\text{Fe}^{3+}$; therefore, in the absence of complications in the mechanism, a faster reaction would be expected. Actually, under similar conditions the oxidation rate constant is indeed about 2.2 times greater than that for Fe^{2+} .

The system I^-/I_2 , beside its immediate use as a redox catalyst, offers the chance to learn more about the reaction mechanism of oxidation by oxygen. This is necessary for the basic understanding of the irreversibility of the oxygen electrode and for any improvement of it.

III. THE DETERMINATION OF CATION ADSORPTION IN THE OXYGEN REDUCTION IN ALKALINE SOLUTION

1. Introduction

The reduction of oxygen on platinum in alkaline solutions occurs through H_2O_2 as an intermediate.⁵ This can be represented as:



It was found that the addition of small quantities of the cations Ca^{++} , Sr^{++} and Ba^{++} changed the rate of the reactions.^{1,6,7} The total reduction current was found decreased several times while the k_2 value increased an order of magnitude.¹ This effect was tentatively explained by the adsorption of the cations on the oxidized platinum surface.⁶ The problem was further investigated by some Russian workers⁸ using radiotracer method to determine the amount of Ca^{++} and Ba^{++} adsorbed on the platinum surface. The effect was explained by the formation of stable compounds between the cations and oxides of platinum. However, the experimental method they used involved some uncertainty in the determined amount. According to their procedures, the adhering solution containing radioactive materials was corrected for by weighing the solution and the electrode together and

then substrating the dry weight of the electrode without counting the evaporation of the solution while weighing. Since the adhering solution is always a problem in the radiotracer method of studying adsorption and there is not any satisfactory method existed at the present for the study of ion adsorption, at relatively high concentrations, there is an urgent need to have a new method developed for this purpose. It is the aim of this work to develop a reliable method for determining ion adsorption and to explain the effect of the cations on the oxygen reduction through the result of the adsorption study. After many considerations and discussions with the experienced workers in this laboratory ellisometry was chosen to be a very promising method for this study.¹⁹⁻¹¹ Ellisometry has long been proven to be a highly accurate and non-destructive method for surface study. It has the advantage of making available a simultaneous study of the electrochemical reaction and the adsorption phenomenon. This method has been developed to study the oxygen-containing films on platinum electrodes¹² and the passivation of nickel¹³ in this laboratory.

2. Experimental

According to other workers,⁸ the maximum coverage of Ba^{++} on platinized platinum is about 15% of a monolayer. In order to see such a small amount of Ba^{++} adsorbed on the electrode surface, an extremely good sensitivity of the ellisometer is required. For this reason, a few modifications have been made to the ordinary ellisometry:

1. A laser is used as the light source to obtain an intense, monochromatic and parallel beam.

2. Multiple reflection is employed to enhance the effect due to the small amount of adsorption.

With these modifications, it is expected that 1% of precision could be obtained in the determination of Ba^{++} adsorption provided that the ellisometer is sensitive to $\pm 0.01^\circ$. Since the sensitivity of the instrument is the major factor governing the success of the experiment, most of the initial effort has been devoted to increase the sensitivity of the ellisometer during this reporting period.

The laser was produced by Optics Technology Inc. (Model 170). The ellisometer used in the experiment is a Gaertner Model L119 (Gaertner Optical Instrumentation.) This instrument is designed primarily for the mercury light source with a wavelength of 5641 \AA .

Two pieces of platinum surfaces made by sputtering technique on glass substrate were used in the preliminary experiments reported here. The two surfaces were made parallel with a distance of 1 mm from each other. The region for the multiple reflection was about 1 cm wide across the surfaces. The experiments were done in air.

The polarizer, quarter-wave plate and analyzer were aligned to $\pm 0.02^\circ$ by first calibrating the analyzer with the reflected light from a quartz surface at the Brewster angle of incidence when the quarter wave plate was removed and then finding the extinction position of the light by turning the polarizer and later the quarter-wave plate when both arms of the instrument were in a straight-through position.

3. Results

It was found from these preliminary experiments that the required

precision is obtainable by using multiple reflection provided that the following conditions are fulfilled:

- (1) The surfaces used in the reflection of light are clean and smooth.
- (2) A small point source of light (with a maximum diameter of 1mm) is impinged upon the surfaces.
- (3) The light doesn't penetrate through the surfaces and cause diffusing light spread around the main reflected beam.
- (4) Since the sensitivity is proportional to the ratio of the change of intensity of light to the change of the position of the quarter-wave plate and analyzer, the reflected light should have the intensity ratio of its maximum to minimum values, obtained by changing the position of the quarter-wave plate and analyzer, to be greater than three orders of magnitude.

Under the above conditions, reflected light from two parallel platinum surfaces at 9 reflections was measured to the sensitivity of $\pm 0.02^\circ$.

4. Plan for the Future

From the results obtained in the preliminary experiments, the following plans were made for the next step of the measurement:

- (1) Freshly prepared, smooth platinum surfaces made by vacuum deposition technique will be used in the measurement.
- (2) Since the quarter-wave plate and photo-multiplier were designed for the mercury light, it may prove necessary to change these parts to the corresponding ones designed for laser beam.

(3) A cell suitable for both electrochemical and optical measurements will be designed and manufactured.

(4) Successive improvement to the equipment as well as to the experimental technique for obtaining better precision will be carried on upon each subsequent experimental result.

(5) Although the ellisometry technique described here is primarily designed for the determination of ion adsorption, there is no good reason to deny its general applicability to the adsorption of any other substances, since there is no special condition concerning the specific property of the system (such as charge, mass, physical state, concentration, etc.) has been imposed upon the technique itself. The success of ellisometry technique in the determination of ion adsorption will serve as a very good starting point in obtaining a general method for adsorption study even for a very small amount adsorbed.

IV. REFERENCES

1. Report No. 4 (1966), U. S. Army Electronics Command, Fort Monmouth, New Jersey, Task No. 1 CO 14501 A34A-00.
2. Report No. 5, U. S. Army Electronic Command, Fort Monmouth, New Jersey, Task No. 1 CO 14501 A34A-00.
3. Report No. 6, U. S. Army Electronic Command, Fort Monmouth, New Jersey, Task No. 1 CO 14501 A34A-00.
4. N. M. Latimer; Oxidation Potentials, Prentice Hall, 1952.
5. Report No. 10 (1964), U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey, Task No. 3A 99-09-001-02.
6. A. Kozawa, J. Electroanal. Chem., 8, 20 (1964).
7. L. Myuller and V. V. Sobol', Elektrokhimiyz, 1, 111 (1965).
8. N. A. Balashova and M. I. Kulezneva, Elektrokhimiya, 1, 155 (1965).
9. K. H. Zaininger and A. G. Revesz, RCA Review, 25, 85 (1964).
10. Ellipsometry in the Measurement of Surfaces and Thin Films, Symposium Proceedings, Washington 1963, U.S. Department of Commerce, National Bureau of Standards, Miscellaneous Publication 256.
11. F. L. McCrackin, E. Passaglia, R. R. Stromberg and H. L. Steinberg, J. Research of the National Bureau of Standards, Vol. 67A, 363 (1963).
12. Report No. 8 (1963), U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey, Task No. 3A 99-09-001-02.
13. B. Rao, Ph.D. Thesis, Department of Chemistry, University of Pennsylvania, 1966.

V. PROJECT PERSONNEL

The following personnel performed the approximate number of man hours of work as follows:

John O'M. Bockris

Estimated 33 man hours

Project Director with academic background in physical electro-chemistry.

B.S. in Physical Chemistry, Imperial College (London)

Ph.D. in Physical Chemistry, Imperial College (London)

D.Sc. University of London

Aleksander Damjanovic

Estimated 300 man hours

Project Supervisor with academic background in physical chemistry and physical metallurgy.

B.S. in Chemical Engineering, Belgrade University.

Ph.D. Cavendish Laboratory, Cambridge University.

Marvin Genshaw

167 man hours

B.S. Chemistry, Michigan College of Mining and Technology.

Ph.D. in Chemistry, University of Pennsylvania.

Darko Sepa

500 man hours

M.S. Ch.M.E., University of Belgrade.

Endre Beer

500 man hours

M.S. Chemistry, Technical University, Hungary, 1956.

Ph.D. Chemistry, Technical Hochschule, Darmstadt, Germany, 1963.

Ying-Cheh Chiu

500 man hours

B.Sc. in Chemical Engineering, Cheng Kung Univ., Taiwan.

Ph.D. in Chemistry, Baylor University.

Technicians

Charles Searles	75 man hours
Henry Hudson	50 man hours
Niel Nathanson	11 man hours
Ray Dolgert	13 man hours

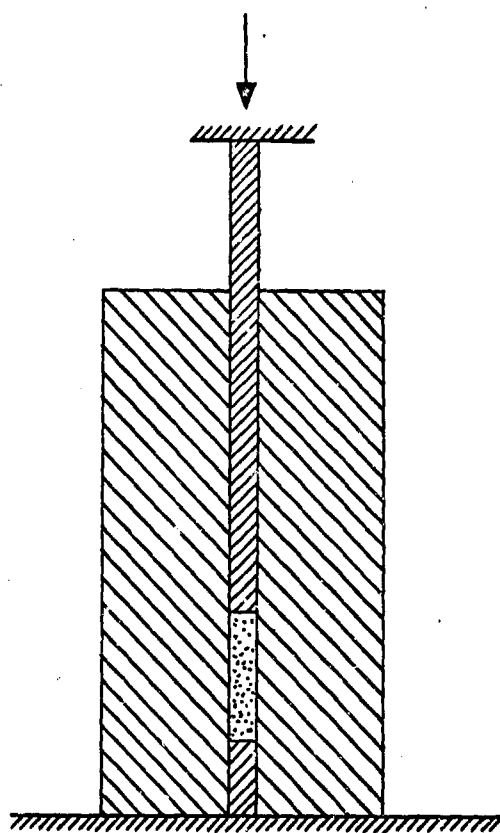


FIG.1 Mold for pressing mixture of gold and bronze powders.

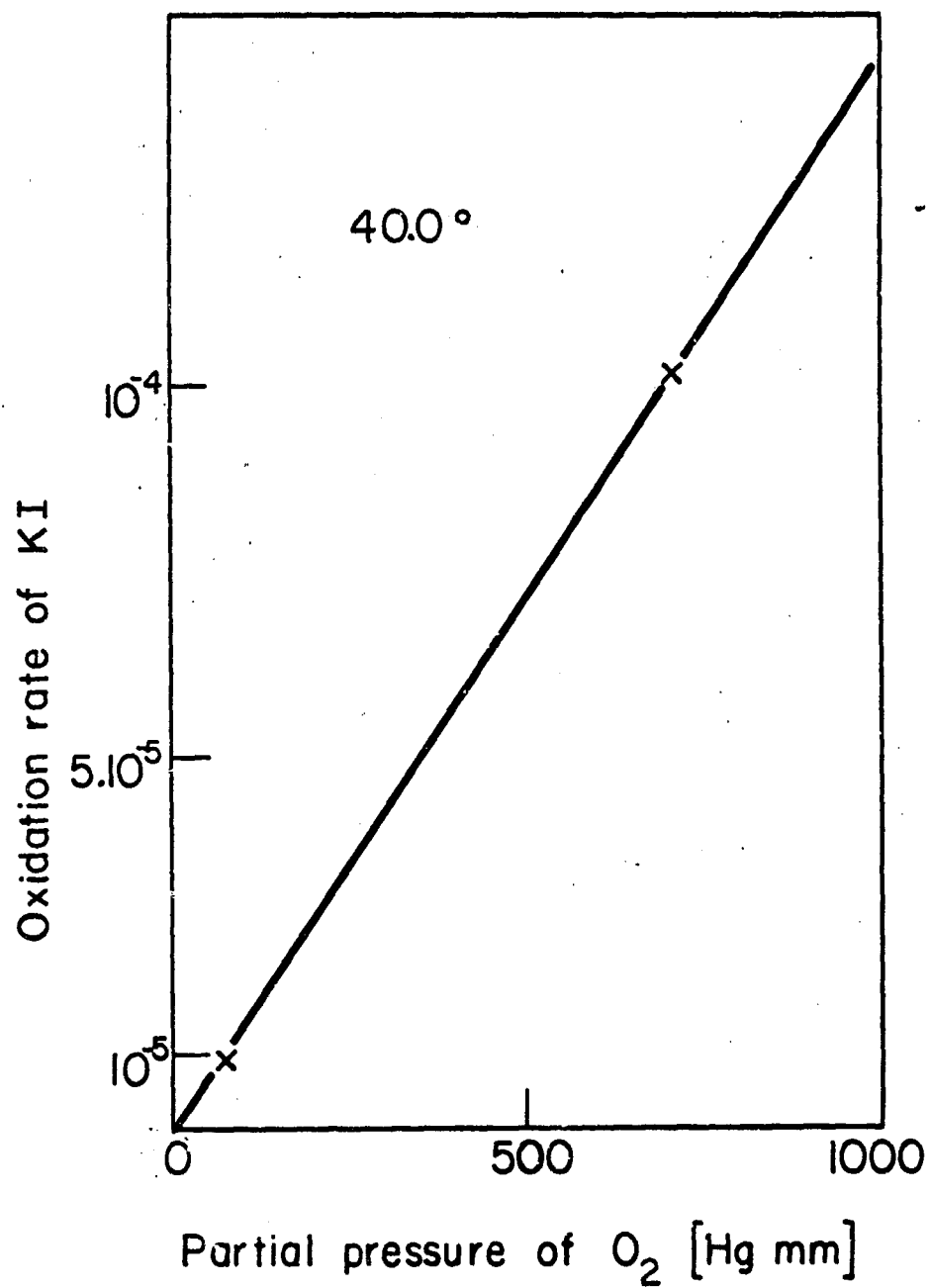


FIG.2 Dependence of reaction on oxygen pressure

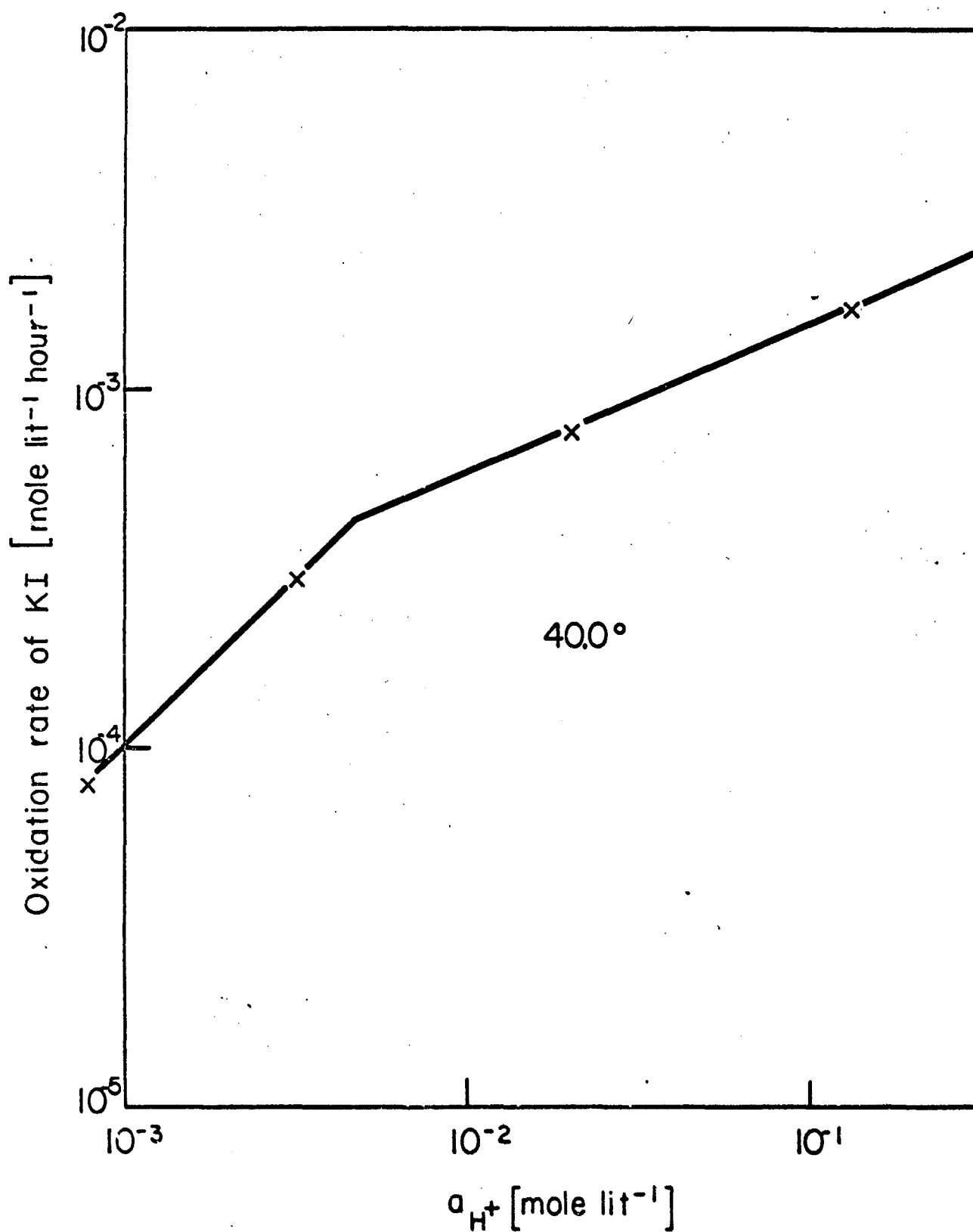


FIG. 3 Dependence of reaction rate on hydrogen ion activity.

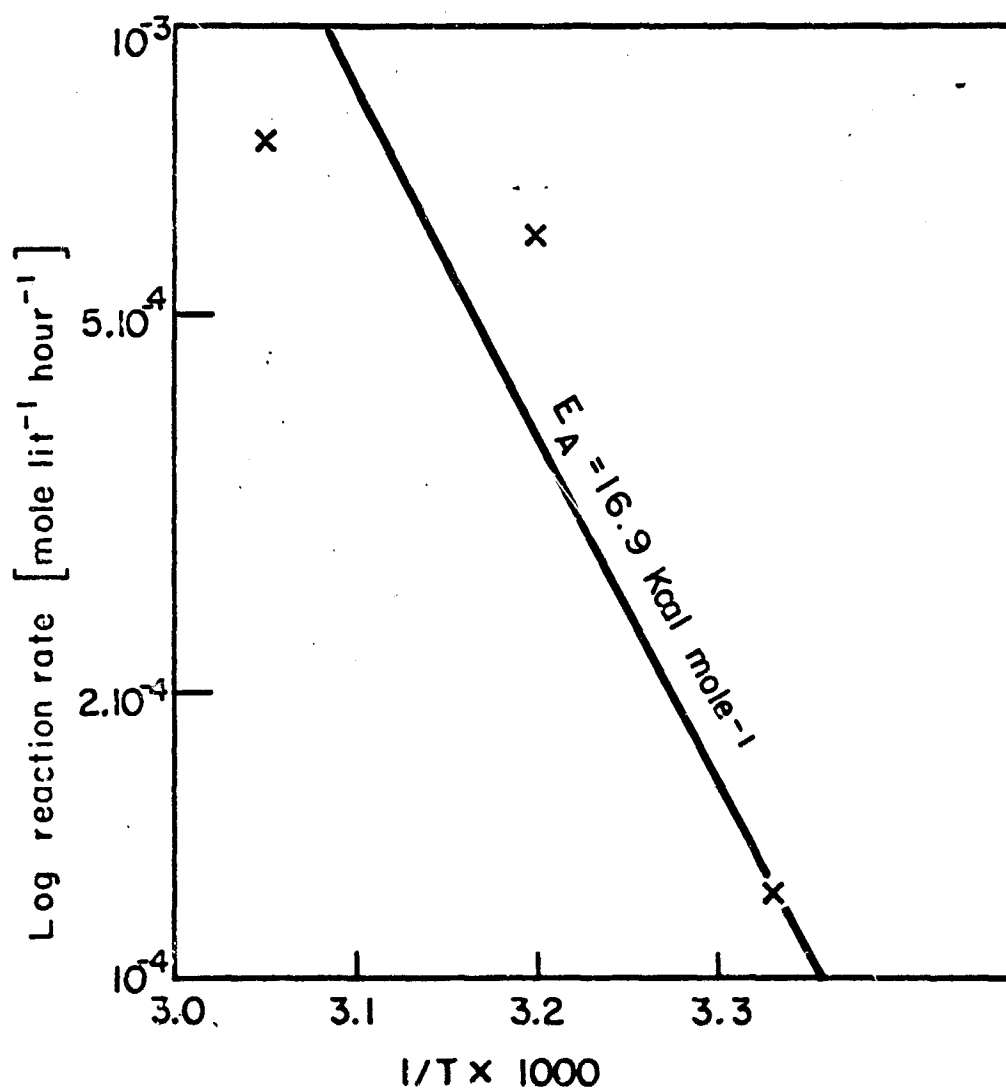


FIG.4 Plot for determining activation energy

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) University of Pennsylvania The Electrochemistry Laboratory Philadelphia, Pennsylvania 19104		2a. REPORT SECURITY CLASSIFICATION Unclassified
3. REPORT TITLE REVERSIBLE OXYGEN ELECTRODES		2b. GROUP
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Quarterly Report 15 Oct 66 - 14 Jan 67		
5. AUTHOR(S) (Last name, first name, initial) Bockris, J. O'M.; Genshaw, M.; Beer, E.A.; Sepa, D. and Chiu, Y.C.		
6. REPORT DATE February 1967	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS 13
8a. CONTRACT OR GRANT NO. DA28-043-AMC-01291(E)		8b. ORIGINATOR'S REPORT NUMBER(S)
a. PROJECT NO. 100 14501 A 34A		8c. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) ECOM-01291-7
c. Task No. -00		
d. Subtask No. -07		
10. AVAILABILITY/LIMITATION NOTICES Each transmittal of this document outside the Department of Defense must have prior approval of Commanding General, U.S. Army Electronics Command, Fort Monmouth, N.J. ATTN: AMSEL-KL-PE		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U.S. Army Electronics Command Fort Monmouth, N.J. ATTN: AMSEL-KL-PE	
13. ABSTRACT Small crystals of lithium, potassium and cesium tungsten bronzes were prepared. Also nonstoichiometric γ -tungsten trioxide was prepared. To study the catalytic activity of these bronzes a method of sintering them into gold was devised. The homogeneous oxidation of iodide by oxygen was studied. The rate constant at 25° is $4 \times 10^{-5} \text{ sec}^{-1}$. The reaction is first order in oxygen and zero order in iodide and hydrogen ions. The activation energy is 16.9 kcal/mole. A very sensitive method of determining ion adsorption utilizing multiple reflection ellipsometry is suggested. (Authors)		

DD FORM 1473 1 JAN 64

Unclassified
Security Classification

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fuel Cell Electrode						
Oxygen Electrode						
Electrode Catalysts						
Oxide Materials (Perovskite Type)						
Tungsten Bronzes						
Redox Couples						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Unclassified
Security Classification